Hydrothermal Stable Templated Molecular Sieve Silica (TMSS) Membranes for Gas Separation

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Abstract

In this work we compare the hydrothermal stability performance of a Templated Molecular Sieve Silica (TMSS) membrane against a standard, non-templated Molecular Sieve Silica (MSS) membrane. The tests were carried under dry and wet (steam) conditions and characterised using pure gases (He, H_2, CO and CO_2) at 1-2 atm membrane pressure drop at 200°C. Single gas TMSS membrane H_2, permeance and H_2/CO permselectivity was found to be 2.05 x 10^{-8} mols.m^{-2}.s^{-1}.Pa^{-1} and 15, respectively. The MSS membrane showed similar selectivity, but increased overall flux. He permeance through membranes decayed at a rate of 4-5 x 10^{-10} mols.m^{-2}.s^{-1}.Pa^{-1} per day regardless of membrane ambience (dry or wet). Although H_2/CO permselectivity of the TMSS membrane slightly improved from 15 to 18 after steam testing, the MSS membrane resulted in significant reduction from 16 to 8.3. In addition, membrane regeneration after more than 50 days resulted in the TMSS membrane reverting to its original permeation levels while no significant improvements were observed for the MSS membrane. Results showed that the TMSS membrane had enhanced hydrothermal stability and regeneration ability.

1.0 Introduction

Purification of H_2 rich streams is a widely used process in industrial processes, and is increasingly being developed at smaller scales for fuel cells application. Polymeric electrolyte membrane (PEM) fuel cells using methanol as a fuel are the current choice for vehicle manufactures worldwide. PEM fuel cells have an on board methanol reforming system which generates H_2, CO_2 and CO. As PEM fuel cells operate at low temperatures (< 120°C), CO even at trace amounts poisons the platinum base catalyst in the anode [1]. Hasegawa et al. [2] reported concentrations of CO as low as 10-100 ppmv, pose a threat to normal and CO tolerant fuel cell catalysts. To remove CO, several technologies are available. Selective oxidation and dense metal membranes can achieve almost 100% removal of CO, but are expensive due to their reliance on precious metals [3]. Molecular Sieve Silica (MSS) membranes for CO removal from H_2 have been looked at by several groups [2, 4, 5] due to their low costs, thermochemical stability and high selectivity. Recently, TMSS materials showed improved structural properties and enhanced hydrophobicity [6, 7].

Membranes derived from sol-gel processes selectively permeate gases based on molecular size, with hydrogen having a smaller kinetic diameter (d_k=2.89Å) diffusing through the membrane while hindering the passage of the large molecule CO (d_k=3.76Å). Wet reformate is typically comprised of H_2O, H_2, CO_2, N_2, CO, so development of a MSS membrane resistant to steam is essential. Giessler et al. [6] observed a great reduction in surface area and pore volume of standard silica xerogels exposed to 96% humidity at 75°C for 50 hours. Thermally treated silica xerogels, templated with short chained surfactants (TMSS) however, were almost unaffected by the same treatment. This was due to the increased presence of siloxane over silanol functional groups in the silica matrix, which are less susceptible to water

attack and hence structural modification. de Vos et al. [8] also successfully increased the hydrophobicity of bulk xerogel samples by employing an organic methyl ligand template, which is also known to control micropore size. They applied this templating method to form an effective MSS membrane, but did not explore steam effects on transport properties. Higgins et al. [9] explored the effect of steam on non-templated membranes and observed a H_2 permeation drop of 60% after 60 hours, where it remained stable for 140 hours, suggesting non-templated membranes become stable after an initial sharp decline. The stability of the membrane under different (eg dry) conditions was not explored.

In this work we investigated the performance of both TMSS and MSS membranes for gas separation, in particular the capability of the membranes to remove CO as a clean up system for fuel cell applications. The hydrothermal stability of the membranes was tested in dry and steam conditions, at different temperatures and pressure regimes.

2.0 Experimental

Asymmetric supported MSS and TMSS membranes were prepared by sanding porous α-Al supports (pore size 0.5-1 μm, porosity of 0.3, supplied by Rojan Ceramics, Australia) to prepare fine smooth surfaces for thin film deposition. The supports were then cleaned in ethanol and dried at 50°C overnight. Films were cast onto the substrates by repeated sol-gel dipping and calcining stages following Diniz da Costa et al. [10]. Substrates were coated with four different films. Each film type had a smaller pore size than the last, graduating to the final thin selective films. This graduation method is adopted to achieve high flux and reproducibility of highly selective membranes. The first film was made of γ-alumina by dip coating in a heat-treated sol comprising of diluted Locron (Clarient GmbH), then calcination at 600°C. The intermediate layer was then cast by dip coating in a diluted silica sol made from the HNO_3 catalysed sol-gel process with tetraethyl ortho silicate (TEOS, Aldrich), EtOH and water, then calcination to 500°C at 1° per minute. Addition of methyl-templated silica, methyl triethoxy silane (MTES, Aldrich), was used in the intermediate layer sol-gel process to control the pore size slightly above that for molecular sieving, ready for the selective thin films. The first selective film was cast by further dipping in another diluted silica sol made from the single-step acid catalysed sol-gel process. Finally, the last selective layer was cast by dip coating in another diluted silica sol made using the two-step acid catalysed sol-gel process. Each selective film was calcined to 500°C, 0.5° per minute. All layers concerned were repeated (dipping and calcination) for good measure to repair defects. This method describes formation of MSS films. TMSS films were made using this method, but with the inclusion of a short-chained surfactant in the sol-gel processes and calcination in vacuum to preserve hydrophobic organic pyrolysis products. This hydrophobic modification to Diniz da Costa et al's method [10] is not repeated here, as it is described in detail in Giessler et al. [6]. Table 1 summarises the layering schedule for both MSS and TMSS membrane films.

Table 1 MSS and TMSS membrane layering schedule

Layer	MSS		TMSS	
	Sol	Calcination conditions	Sol	Calcination conditions
1&2	Al based Locron	Atmospheric	Al based Locron & surfactant	Vacuum
3&4	Methyl templated two-step	Atmospheric	Methyl & surfactant sol-gel	Vacuum
5&6	Single step	Atmospheric	Single step surfactant	Vacuum
7&8	Two-step	Atmospheric	Two-step surfactant	Vacuum

MSS and TMSS were measured for permeance at various temperatures (100 – 200°C) and pressure drops (1 and 2 atm) using pure He, H_2, CO_2 and CO in a dead end permeation apparatus depicted in Figure 1. Slight modifications of the rig allowed membranes to be tested continuously with a synthetic reformate. After long exposure under dry conditions, the membranes were also tested for hydrothermal stability with 34% steam for up to 140 hours at 200°C and 2 atm membrane pressure drop. Single gas H_2/CO permselectivities were used to indicate separation performance by returning the rig to dead-end pure gas setup. Measurement of mixture separation is subject to further work.

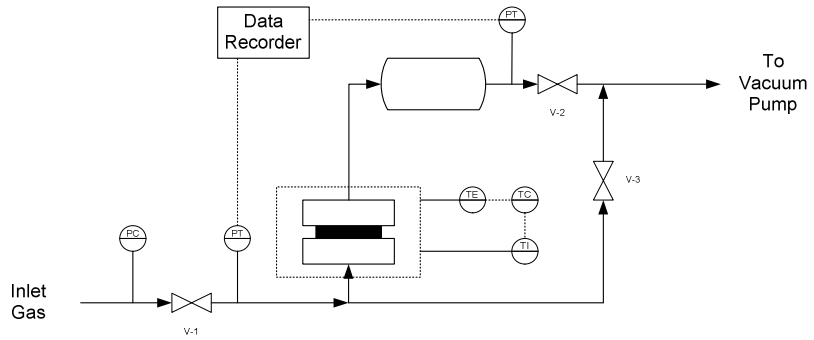

Figure 1 Schematic of dead-end permeation rig

After the prolonged testing period, membranes were then removed and calcined as per their last layer, then returned for testing using single gases. This step was to regenerate the membrane by cleaning off adsorbed components and to observe the irreversible degradation from testing in steam. Membranes were characterised before and after steam testing using He permeance and pure gas H_2/CO permselectivity at 200°C, 2 atm membrane pressure drop.

3.0 Results and Discussion

Permeation results in Figure 2 show that the permeance of all gases increased with temperature, which is characteristic of molecular sieving. One exception to this was CO_2, which decreased. This is in line with other MSS membranes reported in the literature [7, 11, 12]. It is observed the kinetic diameter of the gases tested controlled to a large extent the permeation rates, with the exception of CO (d_k=3.76Å) and N_2 (d_k=3.64Å). This can be attributed to the unique pore size distribution (PSD) of the amorphous silica flim and the relative adsorption properties of the gases. Amorphous thin silica films characterised using nano-permporometry with He [13] showed an initial sharp decline in permeance attributable to closing of 0.5nm pores. After this, permeance tailed off from 0.5 to 1nm pore closures. In our films, there were a small proportion of pores in the membrane matrix that allowed both molecules to diffuse, as the kinetic diameter of both CO and N_2 are very close. In addition, the heat of adsorption of CO (18 $kJ.mol^{-1}$) is higher than that of N_2 (11 $kJ.mol^{-1}$) for MSS, suggesting that CO preferentially adsorbs on the silica surface resulting in higher surface diffusion as per Barrer et al.'s [14] model for activated gas transport in microporous systems. It is also observed that the MSS membrane had a slightly higher permeation than the TMSS membrane.

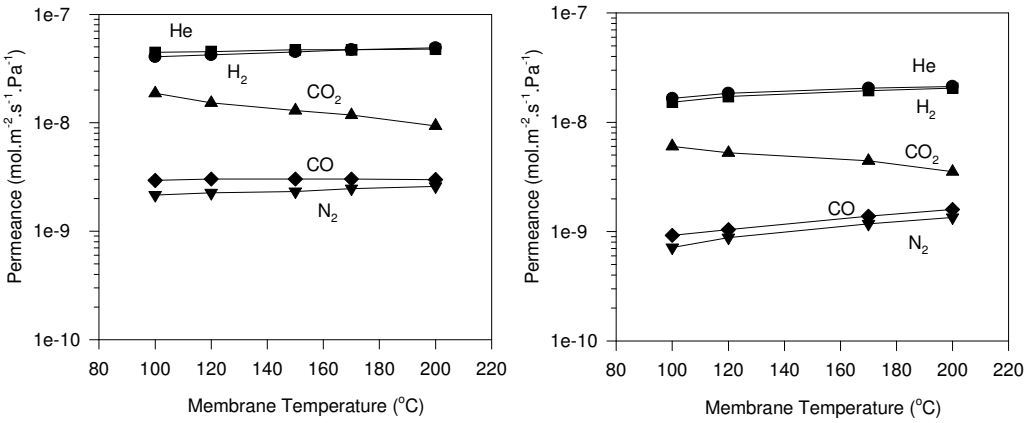

Figure 2 Permeance of gases with membrane temperature at 1 atm membrane pressure drop for MSS membrane (left) and TMSS membrane (right)

The dry and wet stability tests of the membranes for a period of at least 40 days are shown in Figure 3. Both membranes appeared to decrease in He permeance linearly with respect to time, regardless of the exposure conditions, though the TMSS membrane had a slightly higher rate of decay. Both regressions have good fits and very similar slopes. Also, steam testing had almost unnoticeable effect on the He permeance. He permeation decay rates were 4.1×10^{-10} and 4.9×10^{-10} mols.m^{-2}.s^{-1}.Pa^{-1} per day for the MSS and TMSS membranes, respectively. This slight decay in permeance may be attributable to continued ageing of the gel where condensation reactions of surface silanol groups within the pores [15] close them from gas permeation. Nevertheless, after regeneration was carried out (indicated by point 'R' in Figure 3), the TMSS membrane was able to revert to its initial permeation level while the MSS membrane showed almost non-improvement. These results strongly suggest that TMSS membranes are hydrothermally stable and the slow effect of pore closure is less pronounced in the TMSS membrane as there is less proportion of silanol groups in TMSS [16]. In addition, TMSS membranes have great potential for application in fuel cell technology, because regeneration can be carried out in situ.

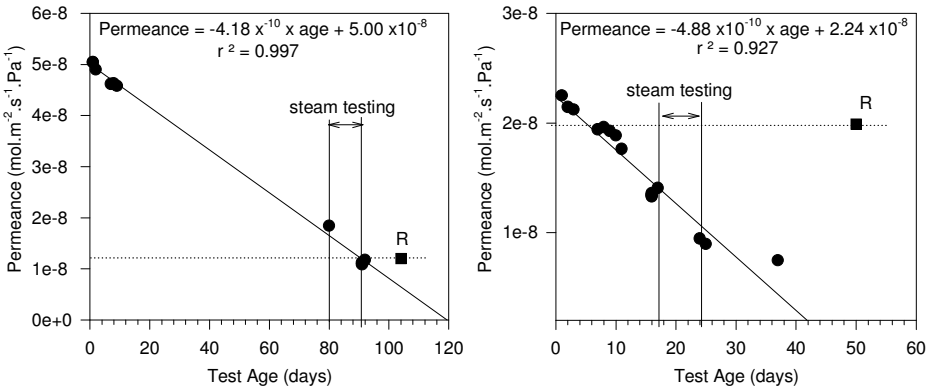

Figure 3: He permeance stability (2atm pressure drop, 200℃) of MSS (left) and TMSS (right) membranes when exposed to various conditions including steam at 200℃. Point 'R' indicates permeance after regeneration.

The dry (before steam), hydrothermal stability (after steam), and regeneration of the membranes for H_2/CO separation capabilities are presented in Table 2. The MSS membrane showed a permselectivity reduction of almost 50% whilst regeneration did not significantly improve H_2/CO separation. The degradation findings for the MSS membrane are in line with previous work reported by Giessler et al. [16], indicating that steam causes micropore widening in non-templated silica membranes, resulting in membranes with lower selectivities. The reduction is mainly attributed to an increased number of silanol groups which easily react with water resulting in film structural changes. On the other hand, steam testing and regeneration of the TMSS membrane seem to slightly enhance H_2/CO permselectivity, suggesting that the templated silica membrane matrix was robust enough to withstand steam, while pore closure due to gradual decay explained above, closed larger pores and therefore increased selectivity with time. Giessler et al. [6] attributed the steam robustness to a large concentration of siloxane bonds and templated carbon elements embedded in the matrix of the membrane. The actual effect of the surfactant in the sol-gel process was not only offer hydrophobicity due to presence of pyrolysed organics, but as it was assisting condensation reactions, producing a hydrophobic microporous siloxane structure.

Table 2: H_2/CO permselectivities (2atm pressure drop, 200°C)

	H_2/CO Permselectivity	
	MSS	**TMSS**
Before steam	16	15
After Steam	8.2	18
Regeneration	8.9	23

The gradual trend in increasing selectivity, even after regeneration, suggests regeneration did not greatly affect the structure. It is possible that while at the high temperatures during regeneration, condensation reactions occurred a little faster within the pores, closing them from the larger gases, hence the increase in permselectivity. More work may be needed to understand this slight increase in selectivity and decay in permeance with time.

4.0 Conclusions

The TMSS membranes derived from surfactant templated sol-gel process showed improved hydrostability as compared to a standard non-templated MSS membranes. The TMSS membrane was able to revert to its initial permeation level after regeneration while H_2/CO permselectivity slightly improved. On the other hand, MSS membranes showed poor hydrothermal stability, resulting in reduction in permeation, even after regeneration, while H_2/CO permselectivity decayed significantly. Therefore, TMSS membranes have a robust structure and the potential to be used as a H_2 purification system in PEM fuel cells application.

5.0 References

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